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Removal of copper and zinc from ground water by granular zero-valent iron: A dynamic freeze–thaw permeable reactive barrier laboratory experiment

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ABSTRACT

Permeable reactive barriers (PRBs) use solution–media interactions for contaminant removal from ground and surface waters. When located in a cold region subjected to freeze–thaw cycling, these liquid–solid phase interactions may be detrimental to PRB performance. This study presents a laboratory based assessment of contaminant removal using granular zero-valent iron (ZVI) under freeze–thaw conditions. Freeze–thaw induced changes to simulated PRBs, contained within Darcy boxes, subjected to 0, 21 and 42 freeze–thaw cycles were assessed using the flow of both reactive and conservative solutions. The reactive contaminants, Cu^{2+} and Zn^{2+} ions, were removed from the pore water during solution flow and freeze–thaw cycling. The hydraulic retention time within the reactive media as assessed by a conservative tracer, decreased by 15–18% after the first set of freeze–thaw cycling and remained constant after the second set of freeze–thaw cycling. A decrease in the uniformity of the particle size distribution and the agglomeration of particles were observed; however there was no change in the hydraulic conductivity within the variance associated with the calculation method. Analysis of the solid particles suggested the contaminant metals were not concentrated in the <212 μm fines that were generated during the experiment. The results obtained suggest that ZVI is suitable for the inclusion in sequenced PRBs for the remediation of metal contaminants in cold regions.

1. Introduction

Zero-valent iron (ZVI) based permeable reactive barriers (PRBs) have been constructed at contaminated sites since the early 1990s (O'Hannesin and Gillham, 1998; Warner et al., 2005). The success of some of these early projects has resulted in the installation of more than 200 PRBs worldwide with 60% of these using ZVI as the reactive media (Henderson and Demond, 2007). As the performance of these barriers continues to be discussed and designs improved, PRBs are becoming an increasingly accepted method for ground water treatment in temperate climates. A major milestone in this process was the publication of the 15-year assessment of the Elizabeth City PRB in North Carolina (Wilkin et al., 2014). This assessment showed that the PRB outlived the chromium plume and continues to treat trichloroethene (TCE) contaminated ground water. However, while these significant investigations have been conducted in temperate climates, research towards the application of PRBs in cold environments has been lacking (Camenzuli et al., 2014).

As operating PRBs consist of water flowing through a permeable material, studies of the impacts of freeze–thaw cycling on PRB media are crucial for the understanding and continued development of this in situ remediation technique for application in areas of freezing ground. The cold-climate PRB longevity concerns of reduced hydraulic conductivity and reactivity are similar to that in temperate climates (see Sections 2.1 and 2.2). Additional challenges due to the climate consist of reduced kinetic rates at low temperatures (Statham et al., under review; Statham et al., in review) and physical particle–solution interactions which can result in particle disintegration and rearrangement during freeze–thaw cycling (see Section 2.3). Previous laboratory freeze–thaw assessments of potential PRB media have consisted of batch testing (Gore et al., 2006b; Li et al., 2002) or measured diesel loaded media permeability (Gore et al., 2006a). If reasonable particle stability during freeze–thaw cycling can be obtained, ZVI may be a favourable additional media for inclusion in PRBs for cold climate applications (Mumford et al., 2013).

This study presents a laboratory based freeze–thaw assessment of contaminant removal using granular ZVI. PRBs are simulated using Darcy boxes and a laboratory incubator. Solution flow changes are monitored at laboratory temperature after 0, 21 and 42 freeze–thaw cycles using both reactive and conservative tracer solutions.

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2. Theory and background

A PRB acts to intercept and treat a migrating contaminant plume. The long term performance and reliability of a PRB is vital in order to provide cost effective treatment. Debate persists concerning the importance of the various mechanisms for the removal of aqueous contaminants by ZVI (Noubactep, 2008; Tratnyek and Salter, 2010). The main contaminant metal removal mechanisms by ZVI are adsorption, precipitation, cementation, co-precipitation and biological processes (Davis et al., 2007; Wilkin and McNeil, 2003). Two major concerns, maintaining hydraulic conductivity and reactivity, may limit the operational lifetime of ZVI PRBs in temperate climates (Henderson, 2010; Jeen et al., 2011; Li et al., 2006). These two properties are interrelated and can result in plume bypass, preferential flow paths, a reduced hydraulic retention time and lower observed reaction rates; all leading to lower contaminant removal efficiencies (Henderson, 2010; Kamolpornwijit et al., 2003). More detail on PRB performance, including a discussion of PRBs which have failed due to construction processes and site specific geochemistry is discussed by Henderson and Demond (2007) and Gavaskar (ITRC, 2011).

2.1. Hydraulic conductivity

Contaminant removal by ZVI is a result of the geochemical conditions generated as the elemental iron core proceeds towards thermodynamic equilibrium. Elemental iron is not thermodynamically stable in contact with water; iron will corrode through solution dependent reactions. The iron oxyhydroxides formed in this reaction process are less dense than the elemental iron core. This can result in a decrease in porosity, an increase in tortuosity, and a reduction in hydraulic conductivity within a PRB (Caré et al., 2013). The corrosion process can also promote the precipitation of secondary minerals from common ions that are found in ground water, form regions of immobile water, and result in gas accumulation from anaerobic oxidation (Henderson and Demond, 2011; Li et al., 2005; Mackenzie et al., 1999; Phillips et al., 2000; Vikesland et al., 2003). Reduced hydraulic conductivity has been observed in many laboratory and field studies. For example, after 20 months of operation at an ammunition plant in Nebraska, a 30 wt.% ZVI in washed local sand PRB experienced a tenfold decrease in hydraulic conductivity (Johnson et al., 2008).

The most common method to attempt to minimise a potential reduction in hydraulic conductivity and also reduce the cost of the reactive media is through combining ZVI with a porous material of constant volume. Typically sand or pea gravel has been used due to the low cost, availability and inert nature of these media (Gillham, 2010). Other possible materials which are more porous or provide the potential for ion exchange or adsorption include compost (Ludwig et al., 2009), pumice (Moraci and Calabrò, 2010), iron slag (Oh et al., 2008), organic fertiliser (Komnitsas et al., 2013) and zeolite (Jun et al., 2009).

2.2. Iron reactivity

The changes to reactions and transport processes within a PRB, and associated reduction of contaminant removal rates are collectively referred to as deactivation or ageing. The precise cause of deactivation is uncertain, however, contributing factors could include the passivation of ZVI due to carbonates and other mineral precipitation blocking reactive sites, diffusion limitations or a declining rate of electron transfer across a growing surface film (Jeen et al., 2007; Ritter et al., 2002).

2.3. Specific cold climate longevity concerns

In addition to the general longevity concerns, PRB design for cold regions must account for reduced kinetic rates and physical particle–solution interactions which can result in particle disintegration and media rearrangement during freeze–thaw cycling. Copper and zinc removal rates by ZVI at a low temperature have been assessed in complementary research (Statham et al., under review; Statham et al., in review). Results at realistic Antarctic conditions showed that the rate of contaminant removal is reduced with a temperature reduction. In water containing oxygen, a temperature reduction from 23 to 4 °C reduces the rate of copper and zinc removal by approximately 35–40%. The removal of copper and zinc from a solution is controlled by film transfer and this diffusion process is slower at lower temperatures.

Freeze–thaw cycling in moist media can result in particle disintegration (Gore et al., 2006b; Murton et al., 2006), frost heave (Bronfenbrener, 2009), particle sorting and patterned ground (Kessler and Werner, 2003). All of these processes can result in changes to the hydraulic conductivity, pore space alteration, preferential flow paths and affect the drainage of water from within a barrier (Fourie et al., 2007).

It is accepted that frost susceptibility, a media particle distribution that promotes capillary movement, increases with increasing fines content and that the mineralogy of the fines is an important consideration. Most frost susceptibility assessments are based on grain size distribution and/or fines content (Chamberlain, 1981). Two well known assessments are Casgrande's (1931) and the No. 200 sieve method (Janoo et al., 1997). By Casgrande's (1931) classification a non-uniform soil is susceptible when the amount of material finer than 0.02 mm is greater than 3 wt.%. The No. 200 sieve method suggests that most materials are susceptible when more than 5–15% of the material passes through a 200 mesh sieve (0.075 mm), where the 5–15% variability is a mean range from different agencies (Janoo et al., 1997).

Another method to assess frost susceptibility is by calculating the saturated moisture holding capacity of the porous media used in a PRB. This can be estimated by using a capillary rise calculation based on the mean particle size as presented by Mumford et al. (2013). Particle disintegration can result in a positive feedback loop where smaller particles are formed, increasing the water holding capacity and hence further increasing the rate of freeze–thaw processes and particle disintegration.

The rate of disintegration of other PRB media in the literature remains unclear. Laboratory testing by Gore et al. (2006b) measured the <250 μm fraction before and after 60 freeze–thaw cycles of granular activated carbon (GAC) and clinoptilolite zeolite. The fines fraction of GAC showed no change, but the proportion of zeolite fines increased from 0.4 to 3 wt.% and ZeoPro fines increased from approximately 1 to 3 vol.%. During a 20 freeze–thaw cycle experiment Li et al. (2002) measured a 1.5 wt.% increase in the <150 μm fraction of an 85 vol.% sand and 15 vol.% clinoptilolite zeolite media. Particle analysis of PRB media extracted after four years of operation at Casey Station Antarctica showed an increase in the fine fraction with depth. This particle size profile was most likely associated with water passing though the lower depths of the media (Mumford et al., 2014). In this field assessment, the average assessed <250 μm mass fraction of GAC, natural Australian zeolite and sand increased from 0.5% to 6%, 0.2% to 4%, and 2% to 4%, respectively. The variations between laboratory and the Antarctic installation are most likely due to the transport of fine particles within or into the field media, the low water flow path within the PRB, the longer time frame of field measurements and higher overburden in the installation due to a greater depth of material.

The PRB media particle size distribution must be selected so that the hydraulic conductivity is higher than the surrounding formation but low enough to achieve an appropriate hydraulic retention time. For cold climate application the PRB media distribution must also be large enough to minimise frost susceptibility and hence capillary rise and the water holding capacity so that during a freezing process the particle–solution interactions do not dramatically alter the particle size distribution or pore space of the media. These changes can reduce the performance of the water treatment process during the subsequent thawing and long-term water flow.